Universidade de Lisboa
Faculdade de Medicina Dentária

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Dissertação

Mestrado Integrado em Medicina Dentária

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orientada pela Professora Doutora Maria Cristina Bettencourt Neves
e coorientada pelo Professor Doutor Jaime Portugal

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Table of Contents

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Resumo

Como consequência da reabsorção contínua e progressiva do rebordo alveolar, a desadaptação da prótese aos tecidos de suporte é frequentemente observada em pacientes portadores de próteses removíveis. Assim, um controlo periódico e rigoroso deve ser realizado para a avaliação da necessidade de um rebasamento. O rebasamento é um procedimento que permite ajustar a base de uma prótese removível aos tecidos de suporte, contribuindo para uma melhor retenção e estabilidade das mesmas. Existem dois métodos para realizar um rebasamento de uma prótese: direto (realizado diretamente na cavidade oral) ou indireto (por intermédio de procedimentos laboratoriais).

As resinas acrílicas autopolimerizáveis têm sido desenvolvidas para serem utilizadas como material de rebasamento, restabelecendo a adaptação e suporte da prótese, permitindo uma maior igualdade na distribuição da carga e contribuindo para a saúde e preservação dos tecidos adjacentes. As resinas para rebasamento direto apresentam uma composição base de pó em polietilmetacrilato (PEMA), enquanto a composição do líquido varia consoante o material, podendo incluir, por exemplo, os monómeros 1,6-hexanedioldimetacrilato (1,6-HDMA) ou isobutilmetacrilato (IBMA). Por seu lado, as resinas para rebasamento por intermédio de procedimentos laboratoriais apresentam uma constituição semelhante às resinas convencionais utilizadas para a base da prótese, com polimetilmetacrilato (PMMA) no pó e metilmetacrilato (MMA) no líquido.

Este material é classificado como um polímero, ou seja, apresenta-se sobre a forma de uma cadeia longa de pequenas unidades repetidas (monómeros). Durante a reação de polimerização das resinas acrílicas, um iniciador, geralmente o peróxido de benzoílo, quebra a ligação dupla do monómero, ficando exposto um local de ligação para o contínuo crescimento da cadeia. Esta conversão de monómeros em polímero nunca é completa e quantidades variáveis de monómero não convertido (monómero residual) permanecem na rede polimérica ou são libertados para o meio circundante.

Apesar de ser o grau de conversão o fator mais importante que determina a quantidade de monómero residual, esta quantidade está dependente de vários fatores, como, por exemplo, o tipo de resina, a composição da mistura, o tipo de reação de

polimerização, a duração do ciclo de polimerização, a natureza do iniciador, a espessura da resina e o tipo de polimento.

De forma a diminuir as alterações das propriedades mecânicas dos materiais e as reações adversas dos tecidos na cavidade oral, como consequência da libertação gradual de monómero residual, foram propostos diversos tratamentos pós-polimerização. Assim, a imersão da prótese num banho térmico com água a 55 ºC ou a radiação com micro-ondas promove a libertação de monómero residual antes da inserção da prótese na cavidade oral.

Mais recentemente foi proposto como tratamento pós-polimerização a imersão de próteses removíveis rebasadas com resinas de rebasamento direto, Ufi Gel Hard e Kooliner, em soluções específicas de etanol a 20% e 50%, respetivamente, aquecidas a 55ºC durante 10 minutos.

Um dos objetivos do presente estudo foi avaliar o efeito do tratamento pós-polimerização com etanol na resistência ao corte de três resinas acrílicas autopolimerizáveis de rebasamento (Kooliner, Ufi Gel Hard e Probase Cold) quando aderidas a uma resina termopolimerizável para base da prótese (Probase Hot). Foi também estudado o efeito do tipo de resina nos valores de resistência ao corte.

Cento e cinquenta espécimes (12×10×6 mm) de resina para base da prótese foram confecionados. Após a polimerização, os espécimes foram submetidos a 2 500 ciclos de termociclagem (5-55 ºC). De seguida, as resinas de rebasamento foram unidas à superfície preparada da resina para base da prótese através de um molde de silicone (5×3 mm). Após a polimerização, os espécimes foram divididos em 5 grupos (n=10) e submetidos a um dos seguintes tratamentos: imersão em água ou em soluções de etanol a 20%, 50% ou 70% a uma temperatura de 55±2 ºC durante 10 minutos. Como controlo, foram utilizados espécimes que não foram submetidos a qualquer tratamento pós-polimerização. Depois do armazenamento em água destilada numa estufa a 37 ºC durante 48 horas, os espécimes de cada grupo foram submetidos a testes mecânicos de resistência ao corte, com uma máquina de testes universal *Instron*, utilizando uma velocidade de 1 mm/min. As superfícies foram observadas com um esteromicroscópio para determinar o tipo de falha, sendo estas classificadas como: adesivas, quando a falha ocorre na interface de adesão, ou mista, quando existiu a combinação de falha adesiva e coesiva da resina acrílica de rebasamento.

Outro dos objetivos foi avaliar o efeito do mesmo tratamento pós-polimerização na energia de superfície das mesmas resinas acrílicas autopolimerizáveis de rebasamento e comparar os valores entre as diferentes resinas acrílicas.

As resinas de rebasamento (Kooliner, Ufi Gel Hard e Probase Cold) foram colocadas no interior de moldes de aço (160×18×1 mm) e, após a sua polimerização, foram seccionadas de forma a obter 75 espécimes (24×18×1 mm). De seguida, os espécimes foram divididos em 5 grupos (n=5) e foram submetidos a um dos seguintes tratamentos: imersão em água ou em soluções de etanol a 20%, 50% ou 70%, a uma temperatura de 55±2 ºC durante 10 minutos. Como controlo, foram utilizados espécimes que não foram submetidos a qualquer tratamento pós-polimerização. Após o armazenamento em água destilada numa estufa a 37 ºC durante 48 horas, utilizando-se a técnica da placa de *Wilhelmy*, no tensiómetro de *Kruss*, os ângulos de contacto foram determinados. A energia de superfície foi posteriormente calculada pelo método de *Wu*.

Os resultados obtidos foram analisados estatisticamente através de testes não paramétricos segundo o método de *Kruskal-Wallis*, seguindo-se múltiplas comparações pelo teste de *Mann-Whitney* com correção *Bonferroni*. Em todos os testes estatísticos foi considerado o nível de significância de 5%.

Não foram encontradas diferenças estatisticamente significativas (p=0.378) entre os valores de resistência ao corte obtidos para os diferentes tratamentos realizados. Os valores de resistência ao corte obtidos com Probase Cold foram estatisticamente superiores (p<0.001) aos valores encontrados com as outras duas resinas testadas. No entanto, não se encontraram diferenças estatisticamente significativas (p=0.714) entre Kooliner e Ufi Gel Hard. Todos os grupos apresentaram somente falhas adesivas.

Relativamente à energia de superfície, todas as resinas apresentaram diferenças entre os diversos grupos testados. Para o material Kooliner, o grupo tratado com água apresentou valores de energia de superfície estatisticamente superiores (p<0.05) ao grupo controlo pelo aumento da sua componente polar. Para o material Ufi Gel Hard, o tratamento pós-polimerização com etanol a 70% demonstrou valores de energia de superfície estatisticamente inferiores, quer pelo aumento da sua componente dispersa, quer pela diminuição da sua componente polar. No Probase Cold, apesar de existirem diferenças nos valores de energia de superfície entre os diferentes grupos, ambas as componentes, dispersa e polar, não demostraram diferenças significativas. Quando comparadas as resinas acrílicas entre si, Ufi Gel Hard apresentou valores mais elevados (p<0.001) de energia de superfície, pelo aumento da sua componente dispersa

(p<0.001), comparado com Kooliner. Enquanto que o Probase Cold demonstrou valores mais elevados (p<0.001) de energia de superfície pelo aumento da sua componente polar (p<0.001), comparando com Kooliner. No entanto, não se encontraram diferenças estatisticamente significativas (p=0.914) entre Ufi Gel Hard e Probase Cold.

Concluindo, o tratamento pós-polimerização com etanol não afeta a adesão entre a base da prótese e as resinas acrílicas de rebasamento, apesar da adesão de Probase Cold ser melhor quando comparada com as outras resinas acrílicas, Kooliner e Ufi Gel Hard.

Em relação à outra propriedade, o tratamento pós-polimerização com etanol não afeta a energia de superfície para Kooliner e Probase Cold. No entanto, para Ufi Gel Hard a energia de superfície foi afetada pelo tratamento pós-polimerização com etanol a 70%. Quando comparadas entre si as resinas acrílicas de rebasamento, Kooliner apresentou valores de energia de superfície inferior a Ufi Gel Hard e Probase Cold.

Dentro das limitações deste estudo, pode-se concluir que o tratamento pós-polimerização com etanol continua a ser um método simples, de rápida aplicação e que não implica custos adicionais para o profissional. É um tratamento eficaz na redução do monómero residual sem prejudicar as propriedades mecânicas das resinas acrílicas de rebasamento.

Palavras-chave: Resistência ao corte, Energia de superfície, Resinas acrílicas, Tratamentos pós-polimerização, Etanol.

Abstract

Immersion of relined dentures in ethanol solutions has been proposed as post-polymerization treatment to increase materials biocompatibility.

The main purpose of this work was to evaluate the effect of ethanol solutions as post-polymerization treatment on the properties of acrylic reline resins (Kooliner, Ufi Gel Hard and Probase Cold): shear bond strength to the denture base resin and the surface free energy.

Shear bond strength test was performed on specimens of reline resins attached to denture base resin, after submitted to water, 20%, 50% or 70% ethanol solutions at 55 ºC for 10 minutes (n=10). Controls were left untreated. After this test, the failure mode was assessed.

Surface free energy was estimated by contact angles determination, performed by the Wilhelmy plaque technique, on specimens submitted to the treatment with ethanol solutions (n=5).

For all resins there were no statistically significant differences (p=0.378) in shear bond strength between groups. However, the Probase Cold showed higher values (p<0.001) than the others. All of the failures were adhesive.

All resins showed differences of surface free energy between groups. For Kooliner the water group showed higher results in surface free energy and its polar component than control group (p<0.05). Considering Ufi Gel Hard, treatment with 70% ethanol solution showed significant lower values in surface free energy and its polar component and higher values in the dispersive component. For Probase Cold specific differences of total surface free energy between groups were not followed by an alteration on their components equilibrium. Kooliner showed lower values (p<0.001) in surface free energy than the other resins.

Ethanol solutions as post-polymerization treatment did not deteriorate the bond strength of acrylic reline resin studied. In general, changes in surface free energy were minimal and not considered clinically relevant.

Keywords: Shear bond strength, Surface free energy, Acrylic resins, Post-polymerization treatments, Ethanol.

1. Introduction

Tooth loss is a significant problem affecting the elderly population (Minami *et al.*, 2004) and, at the moment, an aging population increases the number of edentulous and partially dentate patients (Harwood, 2008). According to a study performed by Douglass *et al.* (2002) in the United States, the number of people who need complete dentures will increase over the next twenty years despite of an anticipated decline in the age-specific rates of edentulism (Douglass *et al.*, 2002). Therefore, the usage of removable dental prostheses, partial as well as complete, will be still a necessity for many people (Kranjcic *et al.*, 2013).

Alveolar resorption, an inevitable consequence of tooth loss, is a continuous and progressive process with resulting loss of fit in local areas of the denture base, because the shape of residual ridges is altered (Reis *et al.*, 2006; Urban *et al.*, 2007b; Kranjcic *et al.*, 2013). In a study done by Tallgren *et al.* (2003), when the resorption progresses over the years, the prosthetic replacement of the lost tissues will give rise to increasing treatment problems and may cause the patient extreme difficulties in managing their dentures (Tallgren, 2003). Therefore, the denture and the ridges should be examined periodically to detect these changes (Leles *et al.*, 2001; Reis *et al.*, 2006).

Relining procedure consists in resurfacing the base of a denture with a new material to fill the space which exists between the original denture contour and the altered tissue contour (Ahmad *et al.*, 2009; van Meegen and Kalk, 2011). It has been described to be an effective procedure for improving the retention, stability and support of the prosthesis (Campanha *et al.*, 2006; Murata *et al.*, 2007; Ohkubo *et al.*, 2009; Neves *et al.*, 2013).

For this purpose some materials may be used, like acrylic resins. Acrylic resins consist of polymeric biomaterials and are frequently used in daily dental practice for diverse functions, like denture base or denture liners. They can be classified as chemical, heat or light activated depending on the factor that promotes the reaction. Chemical or autopolymerizing materials involves a chemical activator like N,N-dimethyl-*p*-toluidine. For heat-activated materials, heat can be generated by hot water bath or microwave energy, while the light-activated uses visible light as energy source (Bettencourt *et al.*, 2010). For relining, a low polymerization temperature is desirable to minimize distortion of the remaining denture base, hence a chemically activated resin

usually is chosen (Phoenix, 2003). Relining with autopolymerizing acrylic resins can be through indirect method in which the denture base is used as individual tray and a functional impression of the tissue is made (Cucci *et al.*, 1996; Yoshida *et al.*, 2013). Alternately, it can be done a direct relining, as it is performed directly in the mouth (chairside) (Machado *et al.*, 2002; Azevedo *et al.*, 2007; Vergani *et al.*, 2010; Yoshida *et al.*, 2013). The composition of indirect reline resins is based on polymethylmethacrylate (PMMA) polymer and methylmethacrylate (MMA) monomer. To be possible to polymerized on the oral cavity, hard chairside reline resins were created and based on polyethylmethacrylate (PEMA), whereas the liquid composition varies among materials and could contain isobutylmethacrylate (IBMA), butylmethacrylate (BMA), 2-hydroxyethylmethacrylate (HEMA) or 1,6-hexanedioldimethacrylate (1,6-HDMA) (Urban *et al.*, 2007a). They also can be hard reline resin or soft lining material (Bettencourt *et al.*, 2010) depending of the amount of plasticizer on their composition.

The polymerization of acrylic resins represents a conversion of low molecular weight molecules (monomers) into high molecular weight macromolecules (polymers) (Urban *et al.*, 2007b). Free radicals created open the double bonds of carbon of monomer and promotes a chain reaction in which the monomer attaches (Cucci *et al.*, 1996). During the polymerization reaction of the acrylic resins, the conversion of monomers to polymers is never complete and some unpolymerized monomers are left in the materials (Campanha *et al.*, 2006; Urban *et al.*, 2007b; Bural *et al.*, 2011; Neves *et al.*, 2013). The residual monomers can be trapped on the polymer matrix, affecting the mechanical and physical properties of the biomaterial, because the residual monomer is a well-known plasticizer (Vergani *et al.*, 2005; Urban *et al.*, 2007a; Urban *et al.*, 2007b; Neves *et al.*, 2013). Also, residual monomer can be diffused into the surrounding medium causing undesirable biological reactions including local chemical irritation, hypersensitivity, mucosal inflammation, vesiculation and ulceration, burning sensation and systemic allergic reactions (Bural *et al.*, 2011; Neves *et al.*, 2013). The amount of residual monomer present depends on the type of resin. Since the residual monomer content is usually higher in autopolymerizing that heat-polymerizing acrylic resins (Lee *et al.*, 2002; Machado *et al.*, 2002; Jorge *et al.*, 2004; Vergani *et al.*, 2005; Bayraktar *et al.*, 2006; Campanha *et al.*, 2006; Urban *et al.*, 2007b). Also, the amount of residual monomer depends on the type of polymerization reaction, the duration of polymerization cycle and the thickness of the material (Jorge *et al.*, 2004).

Over the years the literature has been showing that the amount of residual monomer of acrylic resins can be reduced by post-polymerization treatments such as immersion in water at elevated temperatures (Lee *et al.*, 2002; Urban *et al.*, 2009; Bural *et al.*, 2011) or microwave radiation (Araújo *et al.*, 2002; Vergani *et al.*, 2005; Urban *et al.*, 2007a; Urban *et al.*, 2007b). Tsuchiya *et al.* (1994) recommended the immersion of acrylic resin dentures in hot water (50 ºC for 60 minutes) after polymerization, especially for autopolymerizing resins, with the purpose of minimizing the risk of adverse reactions in patients who wear acrylic resin dentures (Tsuchiya *et al.*, 1994). A study performed by Urban *et al.* (2007) concluded that water-bath and microwave radiation are potential methods to reduce residual monomer content in hard chairside reline resins and improving their mechanical properties and biocompatibility of the relining materials base (Urban *et al.*, 2007a). Due to an increasing concern of the scientific community about the toxicological consequences related to the use of these resins, the search for effective post-polymerization treatments to decrease the residual monomer content has become relevant (Neves *et al.*, 2013).

The effect of ethanol post-polymerization treatment has been investigated. Since 2002, when Bettencourt *et al.* (2002) have decided to study whether immersion in ethanol could be related to an increased liberation of MMA from the polymer matrix of acrylic bone cement used in joint arthroplasty. These authors concluded that ethanol enhances the leaching of the monomer from the polymer matrix (Bettencourt *et al.*, 2002). The effect of different concentrations of ethanol on several properties of a denture base material was evaluated in a study by Regis *et al.* (2009) and the findings of this study showed that ethanol concentrations affects the physical properties of the investigated acrylic resin (Regis *et al.*, 2009). Since water immersion post-polymerization treatment is dependent on temperature (Urban *et al.*, 2009), experiments of Neves *et al.* (2013) also enclosed the possible benefits of the interaction between ethanol aqueous solutions and temperature (Neves *et al.*, 2013). In fact, temperature is known to promote an additional polymerization of the resins and a decrease of residual monomer content (Urban *et al.*, 2007a; Urban *et al.*, 2010; Neves *et al.*, 2013).

Recently, Neves *et. al.* (2013) concluded that, under experimental conditions, a post-polymerization treatment based on a combination approach of ethanol-water solutions and temperature (55 ºC) for 10 minutes enables the reduction of the monomer content and cytotoxicity of acrylic reline resins, without affecting microhardness and flexural strength (Neves *et al.*, 2013).

Adequate bond strength between the two different materials that compose a relined denture is essential for successful clinical performance (Minami *et al.*, 2004; Azevedo *et al.*, 2007; Vergani *et al.*, 2010). The ability of a reline material to bond to an acrylic denture base depends on the chemical composition of the two materials (Ahmad *et al.*, 2009) since the facility of the monomers of the reline material to penetrate into the denture polymer and establish an interwoven polymer network are key elements of this bond (Takahashi and Chai, 2001a; Mutluay and Ruyter, 2005; Azevedo *et al.*, 2007; Vergani *et al.*, 2010; Giampaolo *et al.*, 2011). A weak bond will probably result in adhesive failure under low stress (Azevedo *et al.*, 2007; Vergani *et al.*, 2010) that could result in debonding between the two materials and gap formation with ingress of bacteria and fungus and promote staining (Cucci *et al.*, 1998; Azevedo *et al.*, 2007; Vergani *et al.*, 2010; Giampaolo *et al.*, 2011).

Besides good mechanical strength, surface properties are also crucial for adequate performance of dentures. One of these is the surface free energy, a property that strongly influences the wettability of relining materials which is one of the most important factor that influences the denture retention (Jin *et al.*, 2009). The surface free energy of a solid can be determined by measuring the contact angle (Ozden *et al.*, 1999; Zissis *et al.*, 2001a; Jin *et al.*, 2009). Low contact angle indicates high surface free energy and good wettability and therefore the retention would be expected to be greater (Kilani *et al.*, 1984; Aydin *et al.*, 1997; Ozden *et al.*, 1999; Jin *et al.*, 2009). As the contact angle increases, the surface free energy diminish and wettability decreases (Jin *et al.*, 2009). Poor wettability may lead to frictional problems and patient discomfort (Waters *et al.*, 1999; Jin *et al.*, 2009). Also, along other surface properties such as hardness and roughness, surface free energy contributes to the adherence, bonding and colonization of fungal species. Oral candidiasis associated with prosthetic surfaces is by far considered the most common fungal infection in denture wearers and *Candida albicans* species being the primary etiological agent associated with this infection (Waters *et al.*, 1997; Webb *et al.*, 1998; Moura *et al.*, 2006; de Freitas Fernandes *et al.*, 2011; Al-Dwairi *et al.*, 2012). Studies on denture base materials have shown that there is a strong relationship between the cell numbers of *Candida albicans* adhering and the contact angle measurement (Minagi *et al.*, 1985; Al-Dwairi *et al.*, 2012). Furthermore, other studies concluded that the factor that contributes more to the adherence process is the cell's surface energy, which can be different between species (Waters *et al.*, 1997; Webb *et al.*, 1998).

In spite of the importance of the above properties, the effect of ethanol solutions as post-polymerization treatment on shear bond strength between acrylic reline resins and denture base and on the surface free energy of acrylic reline resins has not been investigated.

2. Objectives

The main purpose of this work was to evaluate the effect of post-polymerization treatment with several ethanol solutions on the shear bond strength of three autopolymerizing acrylic reline resins to one heat-polymerizing denture base resin and on the surface free energy of the reline resins, according to the following hypotheses:

H0: Post-polymerization treatment doesn't affect the shear bond strength between denture base and reline resins.
H1: Post-polymerization treatment affects the shear bond strength between denture base and reline resins.

H0: The acrylic reline resins used don't influence the shear bond strength to denture base resin.
H1: The acrylic reline resins used influences the shear bond strength to denture base resin.

H0: The surface free energy of reline resins isn't affected by the post-polymerization treatment.
H1: The surface free energy of reline resins is affected by the post-polymerization treatment.

H0: The values of surface free energy of the acrylic reline resins are not different.
H1: The values of surface free energy of the acrylic reline resins are different.

3. Materials and Methods

This study evaluated the effect of ethanol solutions as post-polymerization treatment on properties of acrylic reline resins, shear bond strength to the denture base and a surface property, the surface free energy.

Materials used in this study (Appendix 2, Figures 1, 2, 3 and 4) included one heat-polymerizing denture base acrylic resin and three autopolymerizing acrylic reline resins. The name, composition, power/liquid ratio, polymerization condition and manufacturer of the products used in the present investigation are listed in Table 3.1.

Table 3.1 – Materials used in the study.

PRODUCT	***COMPOSITION***		***POWDER/LIQUID RATIO*** *(g/mL)*	***POLYMERIZATION CONDITION***	***MANUFACTURER***	***BATCH NUMBER***
	POWDER	LIQUID				
Probase Hot (PH)	PMMA	MMA	22.5 / 10	Heatpolymerization Heat up to 100 ºC and let boil for 45 minutes	Ivoclar Vivadent AG, Liechtenstein	M36977 (P) L50622 (L) N30391 (SF)
Kooliner (K)	PEMA	IBMA	1.4 / 1	Autopolymerization 10 minutes at room temperature	GC America Inc., Alsip, Illinois, USA	1007201(P) 1008101 (L)
Ufi Gel Hard (UGH)	PEMA	1,6-HDMA	1.77 / 1	Autopolymerization 7 minutes at room temperature	Voco GmbH, Cuxhaven, Germany	1128441 (P) 1134070 (L) 1133100 (CON)
Probase Cold (PC)	PMMA	MMA	1.5 / 1	Autopolymerization 15 minutes at 40 ºC 2-4 bar	Ivoclar Vivadent AG, Liechtenstein	L49853(P) L43809 (L)

P = Powder, L = Liquid, SF = Separating Fluid, CON = Conditioner, PMMA = Polymethylmethacrylate, MMA = Methylmethacrylate, PEMA = Polyethylmethacrylate, IBMA = Isobutylmethacrylate, HDMA = Hexanedioldimethacrylate.

3.1. Shear bond strength

Preparation of denture base specimens

A modified flasking technique was used to make 150 denture base specimens. Rectangular wax specimens (12x10x6 mm) were prepared using a silicon mold. These wax specimens were flasked and placed on top of the investment with gypsum type II. Then, the first layer of gypsum was coated with vaseline and in the upper half of the flask a second mix of gypsum type II (50%) and III (50%) investment was placed and covering the specimens. Before the second layer set, the flask cover was put in place and tapped to fit properly, allowing the excess gypsum to flow out of the holes. After the complete set of the gypsum, the flask was placed in boiling water for 4 to 6 minutes. Then, it was removed from the water and opened for the wax washed away. After elimination of the wax, a separating fluid (Ivoclar Vivadent AG, Liechtenstein) was applied on the gypsum. Thereafter, the heat-polymerizing resin was manipulated, packed into the flask using a hydraulic press and polymerized according to manufacturer's instructions (Table 3.1). The flasks were removed from the water bath and bench cooled to room temperature before specimens were removed.

After the 150 specimens were removed from the molds, their sides were grounded in a rotational grinding and polishing machine (DAP-U, Struers, Denmark) with 600-grit silicon carbide paper (Carbimet Paper Discs, Buehler Ltd., Lake Bluff, IL) under water supply to remove irregularities (Ahmad *et al.*, 2009; Ohkubo *et al.*, 2009).

All denture base specimens were treated by a standardized thermocycling aging procedure of 2 500 cycles thermal fluctuations between 5 ºC and 55 ºC (20 seconds each bath) with 5 seconds of dwell time in a specific machine (Refri 200-E, Aralab, Cascais, Portugal) (Appendix 2, Figure 5).

Relining procedure

Surfaces of denture base specimens were finished to a 3 mm thickness using a rotational grinding and polishing machine (DAP-U, Struers, Denmark) with 600-grit silicon carbide paper (Carbimet Paper Discs, Buehler Ltd., Lake Bluff, IL). This simulates the preparation of the denture base to be relined. The thickness was confirmed with digital micrometer (Mitutoyo Digimatic, MFG.Co., Ltd. Tokyo, Japan) with precision ± 0.01 mm.

The 150 denture base specimens were randomly divided into three groups, corresponding to the three different acrylic reline resins. To customize and define an area of 3 mm in diameter, a perforated adhesive tape (Glossy White Film EA, Xerox) was positioned on the center of the surface of denture base providing a uniform bonding area. As recommended by the manufacturer, specific adhesive was applied on the denture specimen's surface and let it dry in the air (30 seconds) when relined with Ufi Gel Hard. With the Kooliner or Probase Cold specimens, the bonding sites were wetted with the corresponding monomer. Then, a silicon mold having a circular opening (5 mm internal diameter × 3 mm height) was placed over the adhesive tape (Figure 3.1) and each acrylic reline resin was mixed and applied according to the manufacturer's instructions (Table 3.1) (Figure 3.2). With direct relining materials, polymerization was carried out at 37 ºC to simulate the temperature of the oral cavity during the specific time as recommended by the manufacturer (Table 3.1). For the indirect relining material, an Ivomat pressure device (IvoclarVivadent, Lichenstein) was used to maintain 40 ºC and 2-4 bar for 15 minutes (Table 3.1) (Appendix 2, Figure 6).

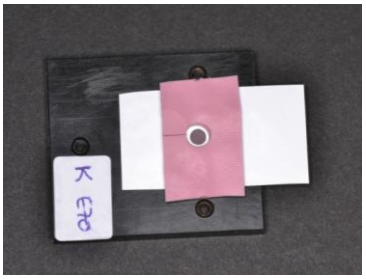

Figure 3.1 – Shear bond strength device with adhesive tape and silicon mold.

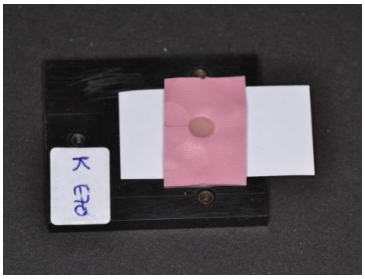

Figure 3.2 - Shear bond strength device filled with Kooliner.

Ethanol post-polymerization treatment

The 50 constructed specimens of each reline resin were randomly divided into five groups (*n*=10) of post-polymerization treatment. Each specimen was exposed to 5 mL of water or ethanol/water solutions of 20, 50 and 70% (V/V) at 55±2 ºC in closed plastic flasks for 10 minutes. The control specimens of the reline resins (C) were exposed to dry conditions at room temperature (no treated).

After submitted to the post-polymerization treatment, specimens were stored in distilled water at 37±2 ºC for 48±2 hours in an incubator (Memmert, Schwabach, Germany) before shear bond strength tests.

Shear bond strength test

Specimens were included in a single plan lap shear bond strength device with gypsum type III (Figure 3.3) (Seabra *et al.*, 2014) and tested in an universal testing machine model 4502 (Instron Ltd, Bucks, HP 12 3SY, England) (Figure 3.4a). Shear bond strength was determined with 1kN load cell and a crosshead speed of 1 mm/min until debonding of the materials (Figure 3.4b) (Watanabe *et al.*, 2000). All tests were performed under uniform atmospheric conditions at room temperature.

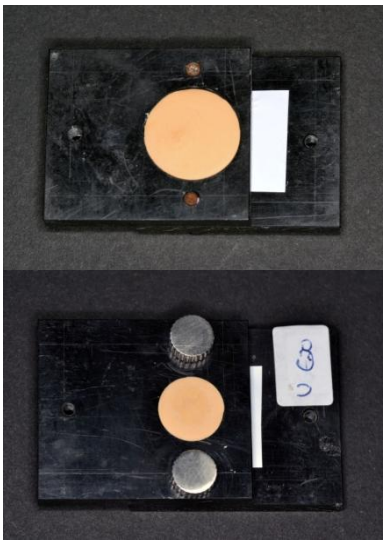

Figure 3.3 – Shear bond strength device with gypsum.

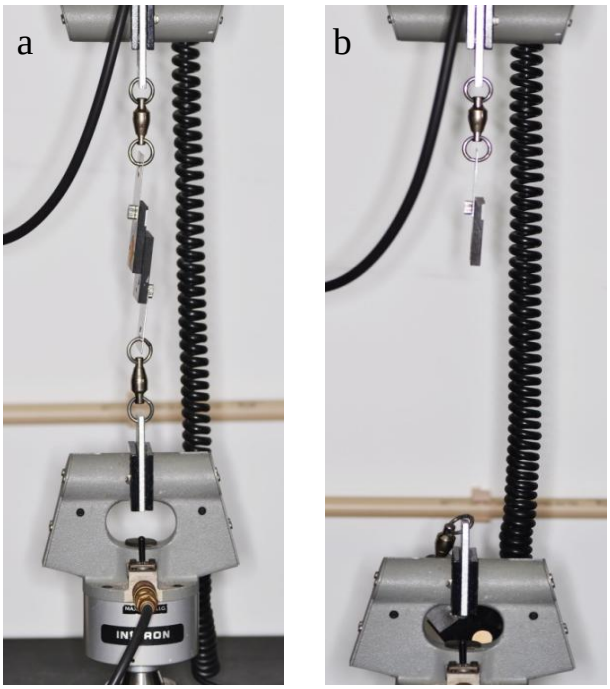

Figure 3.4 – One example of specimen submitted to shear bond strength test in an universal testing machine. a) Before test; b) After test.

Failure Mode

After shear bond testing for all specimens (Figure 3.5), failure mode was analyzed with a stereomicroscope (EMZ-8TR, Meiji Techno Co, Saitama, Japan). The failure was classified by 2 independent observers as adhesive, if the failure occurred at the adhesive interface, or mixed, when a combination of adhesive and cohesive failure in the acrylic reline resin was observed.

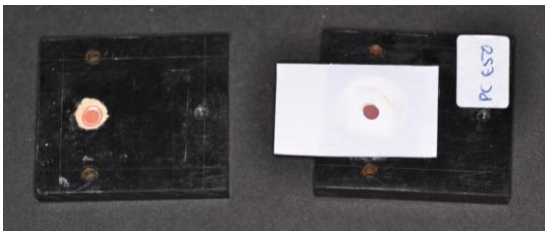

Figure 3.5 – Shear bond strength device after submitted to shear bond strength test.

3.2. Surface free energy

Preparation of specimens

Each acrylic reline resin (Kooliner, Ufi Gel Hard and Probase Cold) specimen was obtained by packing the mixed material into rectangular metal molds (160×18×1 mm) and then each mold was clamped together in order to displace any material's excess (Figure 3.6). After the polymerization with specific conditions according to the manufacturer's instructions (Table 3.1) (Figure 3.7), 25 rectangular specimens of each resin with approximate dimensions of 24 mm width, 18 mm height and 1 mm were obtained from the cured strips. The edges of each sample were polished manually with 600-grit silicon carbide paper (Carbimet Paper Discs, Buehler Ltd., Lake Bluff, IL) in order to remove irregularities.

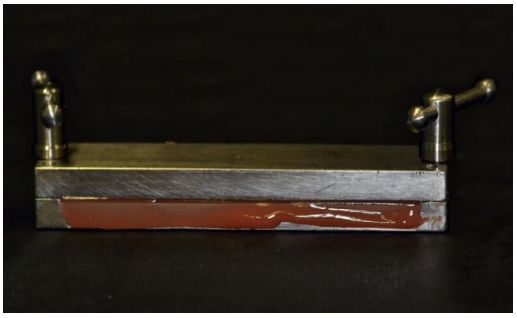

Figure 3.6 – Compression of one resin's dough in the metal mold.

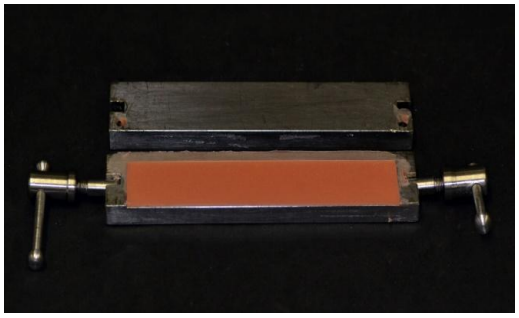

Figure 3.7 – Metal mold opened after polymerization of acrylic reline resin.

Ethanol post-polymerization treatment

The 25 specimens of each material were randomly divided into five groups (n=5) of post-polymerization treatment. Each specimen was exposed to 5 mL of water or ethanol/water solutions of 20, 50 and 70% (V/V) at 55±2 ºC in closed plastic flasks

for 10 minutes. The control specimens of the reline resins (C) were exposed to dry conditions at room temperature (no treated).

The specimens were stored in distilled water at 37±2 ºC for 48±2 hours in an incubator (Memmert, Schwabach, Germany) before setting the contact angle and surface free energy.

Surface free energy determination

To determine the surface free energy of the acrylic reline resin specimens, contact angles of distilled water and 1,2-propanediol were measured on 5 specimens from each group by using Wilhelmy technique (Bettencourt *et al.*, 2004).

Testing was carried out using a Processor Tensiometer K12 (Kruss, Hamburg, Germany) linked to a computer and the advancing and regression contact angle were measured (Appendix 2, Figures 7, 8, 9 and 10).

The system was set in a "Perspex®" box to ensure an artificially controlled environment. A glass cuvette containing the liquid was placed in a steel container with thermostatic circulating water (25±1 ºC). Before each change of the liquid, the cuvette glass was carefully washed with water and acetone mixture and was further assed into the flame of a Bunsen burner to reduce the likelihood of surface contamination.

First, the specimen's dimensions (height, width and thickness) were measured with digital micrometer (Mitutoyo Digimatic, MFG.Co., Ltd Tokyo, Japan) with precision ± 0.01 mm and introduced in the software. At the beginning of each experiment, specimen of acrylic reline resin was suspended in the balance (sensitivity equal to 10^{-4} g) of the equipment. A motorized platform allowed the immersion of 4 mm of specimen in the liquid under study (water or 1,2-propanediol) at a speed of 20 μm s^{-1} (Figures 3.8 and 3.9). In all the procedure, care was taken handling the specimens to reduce the chance of contamination of their surfaces.

Advancing contact angles were used for surface free energy (γ) estimation of all specimens, as well as its dispersive (γ^d) and polar components (γ^p) based on the harmonic mean method proposed by Wu (1971) (Wu, 1971). Equations for surface free energy estimation were solved using the equation handling KRUSS-software program: contact angle measuring system K121 (version 2.049) (Appendix 2, Figure 11).

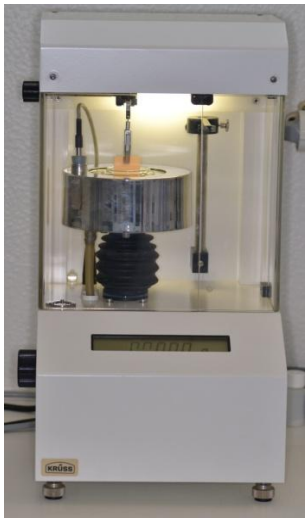

Figure 3.8 – Specimen of acrylic reline resin suspended in the balance of the equipment.

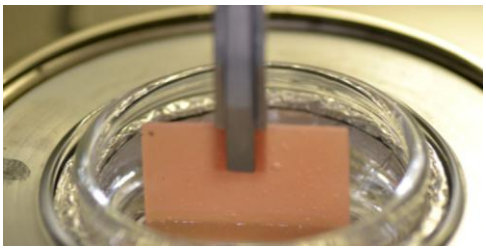

Figure 3.9 – Specimen of acrylic reline resin immersed in the glass cuvette with distilled water.

3.3. Statistical analysis

Data were statistically analyzed using SPSS Statistics 20 (SPSS Inc., Chicago, IL, USA). Data did not follow a normal distribution (verified by a Kolmogorov-Smirnov normality test) and were submitted to nonparametric tests according to Kruskall-Wallis method followed by multiple comparisons using Mann-Whitney tests with Bonferroni correction to determine whether there were specific significant differences among materials and groups.

In all statistical tests, it was considered the 5% level of significance ($p<0.05$).

4. Results

4.1. Shear bond strength

The results of the shear bond strength test are summarized in Table 4.1, where the mean, standard deviation, minimum and maximum values of the groups were registered.

Table 4.1 – Shear bond strength data by reline resins.

MATERIAL	*POST-POLIMERIZATION TREATMENT*	*n*	*SHEAR BOND STRENGTH (MPa)*		
			M ± SD	*MIN*	*MAX*
Kooliner	**Control**	10	5.17±2.11	2.56	7.78
	Water	10	5.35±2.02	2.74	7.96
	Ethanol 20%	10	5.58±2.41	2.97	8.19
	Ethanol 50%	10	5.96±2.38	3.35	8.57
	Ethanol 70%	10	8.10±4.52	5.49	10.71
		50	6.03±2.93		
Ufi Gel Hard	**Control**	10	6.61±2.69	4.00	9.22
	Water	10	4.77±2.40	2.16	7.38
	Ethanol 20%	10	5.16±2.40	2.55	7.76
	Ethanol 50%	10	6.44±3.20	3.83	9.05
	Ethanol 70%	10	8.41±2.21	5.80	11.02
		50	6.28±2.81		
Probase Cold	**Control**	10	14.67±6.75	12.06	17.27
	Water	10	15.12±6.37	12.51	17.73
	Ethanol 20%	10	15.51±6.75	12.90	18.12
	Ethanol 50%	10	15.05±4.49	12.44	17.66
	Ethanol 70%	10	13.49±5.90	10.88	16.10
		50	14.77±5.90		

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

No significant differences in shear bond strength between post-polymerization treatments were found (p=0.378) (Figure 4.1).

However statistical differences (p<0.001) were found between resins. No statistical differences (p=0.714) were observed between Kooliner and Ufi Gel Hard specimens, but Probase Cold showed significantly higher (p<0.001) shear bond strength than the other two resins (Figure 4.2).

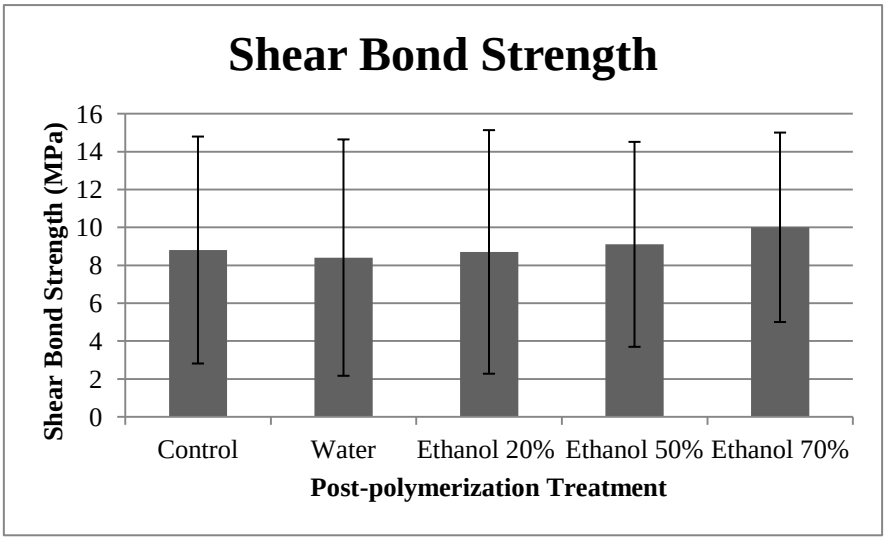

Figure 4.1 – Mean and standard deviation of values of shear bond strength (MPa) of experimental groups.

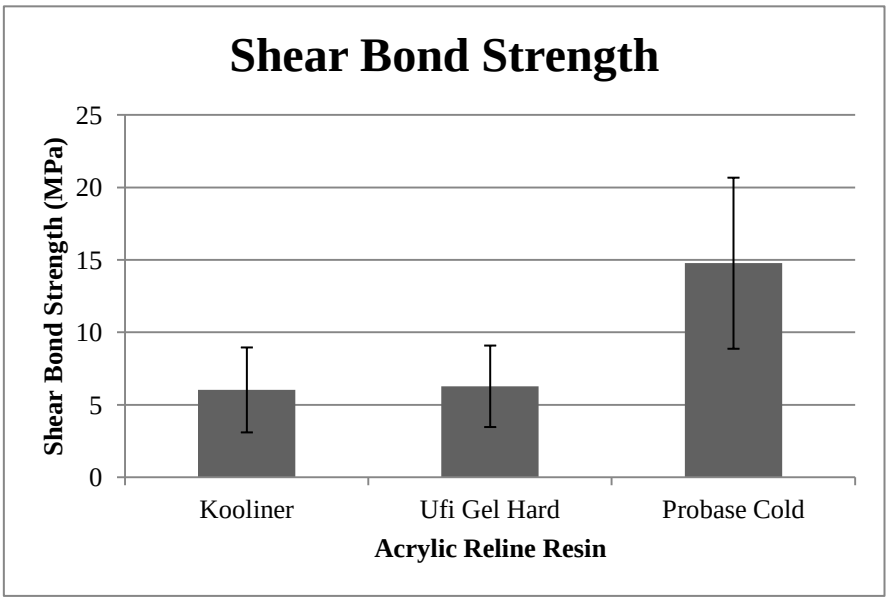

Figure 4.2 – Mean and standard deviation of values of shear bond strength (MPa) of experimental groups.

After analyzes of acrylic resin surfaces, it was found that all specimens showed adhesives failures.

4.2. Surface free energy

For each material, the descriptive analysis of the data was carried out, including mean, standard deviation and minimum and maximum values for contact angle (Appendix 1, Tables 1, 2 and 3) and surface free energy (Appendix 1, Tables 4, 5 and 6).

The values of the total surface free energy (γ) and their components, the dispersive (γ^d) and polar (γ^p), are summarized in Table 4.2, 4.3 and 4.4, where the mean and standard deviation values of the groups by the reline resin were registered.

Considering Kooliner specimens (Table 4.2), a statistical significant differences (p=0.015) in total surface free energy were found between post-polymerization treatments. Specimens treated with water showed significant higher (p=0.040) values than the control group. In the dispersive component, there were no significant differences (p=0.113) between groups, but significant differences (p=0.018) were found in the polar component, where the water group also showed higher (p=0.023) values than the control group.

Table 4.2 – Mean and standard deviation (M±SD) values for surface free energy of Kooliner.

γ (mN/m)	*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
γTotal	32.93±1.72^{A}	36.68±1.77^{A}	33.17±1.32^{B}	33.70±1.50^{C}	35.89±1.67^{D}
γDispersive	17.46±1.89^{A}	16.33±0.68^{B}	16.96±0.86^{C}	18.21±0.95^{D}	18.26±1.84^{E}
γPolar	15.47±2.80^{A}	20.34±2.30^{A}	16.22±1.75^{B}	15.49±1.80^{C}	17.63±1.99^{D}

Horizontally identical superscripted capital letters denote significant differences among groups (p<0.05).

For Ufi Gel Hard specimens (Table 4.3), the total surface free energy showed significant differences (p=0.007) when post-polymerization treatments were compared. Specimens treated with 70% ethanol showed significant lower (p=0.040) values than the control group. In dispersive and polar component, there were significant differences (p<0.05) between groups, with 70% ethanol group presenting significant higher values in the dispersive components and significant lower values in the polar component (p<0.05).

Table 4.3 – Mean and standard deviation (M±SD) values for surface free energy of Ufi Gel Hard.

γ (mN/m)	*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
γTotal	42.55±3.61^{A}	42.61±2.62^{B}	39.74±2.61^{C}	37.26±0.63^{D}	37.26±1.65^{A}
γDispersive	20.98±1.57^{A}	19.43±0.96^{B}	19.66±2.54^{C}	20.91±1.82^{D}	27.71±2.10^{BC}
γPolar	21.57±4.83^{A}	23.19±3.25^{B}	20.08±0.96^{C}	16.35±2.24^{D}	9.55±3.48^{AB}

Horizontally identical superscripted capital letters denote significant differences among groups (p<0.05).

For Probase Cold specimens (Table 4.4), means of groups of post-polymerization treatment in total surface free energy showed differences that were considered statistically significant (p=0.024). The 70% ethanol yielded significant higher (p=0.046) surface free energy than 20% ethanol. In dispersive and polar component there were no significant differences (p>0.05) between groups.

Table 4.4 – Mean and standard deviation (M±SD) values for surface free energy of Probase Cold.

γ (mN/m)	*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
γTotal	38.41±1.16^{A}	38.79±2.70^{B}	37.87±1.21^{C}	40.57±2.02^{D}	42.36±2.33^{C}
γDispersive	18.05±2.06^{A}	18.82±1.18^{B}	18.09±1.97^{C}	18.73±1.47^{D}	19.77±1.34^{E}
γPolar	20.36±2.73^{A}	19.97±3.40^{B}	19.79±1.76^{C}	21.83±3.27^{D}	22.58±2.65^{E}

Horizontally identical superscripted capital letters denote significant differences among groups (p<0.05).

A statistical (p<0.001) influence of the acrylic reline resin in the surface free energy was found (Figure 4.3). Kooliner's total surface free energy was significantly (p<0.001) lower than the total surface free energy of Ufi Gel Hard and Probase Cold. No differences were found (p=0.974) between Ufi Gel Hard and Probase Cold. In dispersive component Kooliner showed statistically lower (p<0.001) values than Ufi Gel Hard and in polar component statistically lower values (p<0.001) than Probase Cold.

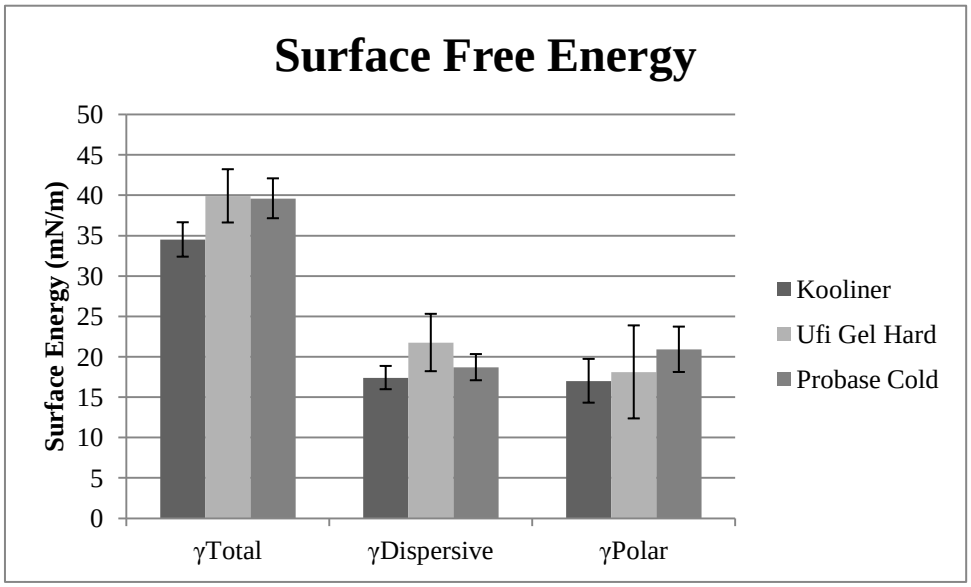

Figure 4.3 – Mean and standard deviation of values of surface free energy (mN/m) of experimental groups.

5. Discussion

Since Neves *et al.* (2013) showed that ethanol post-polymerization treatment was considered an easy and effective treatment to reduce residual monomer and therefore to decrease biological effects, it was important to test the effects of this treatment on the unstudied properties of acrylic reline resins, bond strength to the denture base and the surface free energy (Neves *et al.*, 2013).

In order to full field this requirement, one objective of the present work was to evaluate the effect of ethanol solutions as post-polymerization treatment on the bond strength between three acrylic reline resins (Kooliner, Ufi Gel Hard and Probase Cold) and a denture base resin (Probase Hot).

According to the current literature, there is no general agreement about the most precise method to be used for evaluation of the bond strength of relining materials (Mutluay and Ruyter, 2005). In the present study a shear bond strength test was used. Shear bond strength test has been widely used in acrylic resins, since it represents a shear load directly to the reline-denture base polymer interface and therefore considered more accurate to what happens in the oral cavity compared to the tensile load test (Stipho and Talic, 2001; Takahashi and Chai, 2001a; Takahashi and Chai, 2001b; Minami *et al.*, 2004; Sarac *et al.*, 2005; Mariatos *et al.*, 2006; Neppelenbroek *et al.*, 2006; Azevedo *et al.*, 2007; Ahmad *et al.*, 2009; Vergani *et al.*, 2010; Al Rifaiy, 2012). Others advantages of this test are the simplicity of the specimen's preparation and the capacity of easily align the specimen in the machine without creating deleterious stress distribution (Placido *et al.*, 2007).

The results of the present study showed that there were no differences in shear bond strength between water and the 20%, 50% or 70% ethanol solutions as post-polymerization treatment compared to control in the three acrylic reline resins.

Neves *et al.* (2013) found decreased in the flexural strength and no alteration of hardness in Kooliner or Ufi Gel Hard when post-polymerization treatments with ethanol solutions were done (Neves *et al.*, 2013). According to earlier studies from Seo *et al.* (2007) and Urban *et al.* (2009), the surface properties of the materials were not influenced by the post-polymerization treatments, like hot water or microwave irradiation, and these facts suggest that the effect of post-polymerization treatments is

more pronounced in the bulk of the specimens rather than in their superficial layers (Seo *et al.*, 2007; Urban *et al.*, 2009). In the present study this finding is corroborated because the post-polymerization treatments with ethanol solutions didn't altered significantly the bond strength, considered to be a property attributed to the most superficial layers of a resin.

At this point it may be conclude that the first hypothesis of this study couldn't be rejected, since it wasn't found any effect of the post-polymerization treatment in the bond strength between denture base and acrylic reline resins.

In the present study, Probase Cold showed significant higher bond strength compared to the other resins. This result was already proven in earlier studies since PMMA based reline resin demonstrated significantly higher bond strength to PMMA based denture base resin, compared with non-PMMA-based reline resin (Sarac *et al.*, 2005; Ahmad *et al.*, 2009). Also, no differences were found between Kooliner and Ufi Gel Hard on shear bond strength.

These findings corroborate the theory that bond strength is dependent on the chemical composition of both materials, defended previously by others authors (Arima *et al.*, 1996; Cucci *et al.*, 1999; Leles *et al.*, 2001; Stipho and Talic, 2001; Takahashi and Chai, 2001b; Minami *et al.*, 2004; Ahmad *et al.*, 2009). Bonding of autopolymerizing resins to denture base resin seems to be achieved by penetration and diffusion of monomer into denture base resin. As so, a monomer with smaller molecular weight (like MMA monomer that weights approximately 100 g/mol) may be advantageous for bonding then a heavier monomer (like 1,6-HDMA monomer with 254 g/mol) (Minami *et al.*, 2004). This fact suggests that greater crosslinking occurred between similar base materials. Another monomer with higher molecular weight is IBMA, monomer available in Kooliner, which might have limited monomer penetration (Ahmad *et al.*, 2009). This supported the theory that, when compared with conventional polymers based on methylmethacrylate, the bond strength of hard denture reline resins could not be so effective because of the low penetration of the monomers with relatively greater molecular weight (Arima *et al.*, 1996; Minami *et al.*, 2008; Giampaolo *et al.*, 2011).

An aspect that strengths the present study was innovative approach of the denture based specimens being submitted to a process of ageing. The earlier studies use simply techniques for simulating the usage of a denture before the reline procedure, like

immersion of the specimens for 48 hours (Stipho and Talic, 2001; Urban *et al.*, 2007a; Hasan, 2009). In the present study, ageing was performed by thermal cycling. This is a laboratory process where the specimens are immersed in almost extreme temperatures baths: 5 and 55±2 ºC with a dwell time of 20 seconds (Minami *et al.*, 2004; Giampaolo *et al.*, 2011). Thermal cycling is *in vitro* test from what really happens on the oral cavity, because, in clinical use, the temperature that the denture base can suffer may vary considerably through the intake of hot and cold food and drinks or the use of warm or hot water in cleaning (Neppelenbroek *et al.*, 2006). The literature described that 10 000 cycles of cyclic thermal stressing correspond to a 1-year period of intraoral conditions (Gale and Darvell, 1999), so 3 months of intraoral conditions were simulated by a 2 500 cycles protocol. This was considered the minimal duration for performing a denture evaluation and need for replacement of its base by a relining procedure.

At this point it was possible conclude that the second hypothesis of this study could be rejected, since Probase Cold showed higher shear bond strength to denture base resin than the other resins.

Another objective of the present work was to evaluate the effect of post-polymerization treatment based on ethanol solutions on the surface free energy of the same three acrylic reline resins.

The analysis of the surface free energy was done through an indirect method since contact angle measurements were necessary to calculate the surface free energy. This method is relatively inexpensive, rapid, sensitive and as a wide application in studies of characterization of surfaces of solids (Buckton, 1995). Since it is impossible to directly determine the surface free energy of a solid, it was necessary to resort to determination of the contact angles between the specimens of biomaterial and two liquids, one with a polar nature (water) and a non-polar nature (1,2-propanediol).

There are two ways to determine contact angle: static and dynamic technique. The static sessile drop technique involves the measurement of contact angles formed by a drop of liquid on the investigated material. Difficulty in determining the precise point of contact between the edge of the liquid drop and the surface of the material leads to inaccuracies. Variations in reading will also occur because of drop evaporation, unless measurement is performed in a chamber saturated with vapor (Waters *et al.*, 1999). More recently, the dynamic contact angle analysis technique (Wilhelmy technique) has been introduced, showing advantages in the surface measurement evaluation regarding

the simplicity of the technique and the minimal measurement errors (Waters *et al.*, 1999; Zissis *et al.*, 2001a). Furthermore this technique is quick, reliable (Zissis *et al.*, 2001b) and very precise since does not depend on the subjectivity of the operator, allowing the analysis of a considerable surface area (Neumann and Spelt, 1996). So, this technique was used to compare the surface property of materials in the present study as well as in earlier studies (Sipahi *et al.*, 2001; Zissis *et al.*, 2001a; Bettencourt *et al.*, 2002; Bettencourt *et al.*, 2004). Also, it was able to calculate the advancing contact angle, determined when the board is in the liquid and the contact angle retraction. Although both the values of the contact angle could be considered in the calculation of surface free energy, it is demonstrated that the retraction angles reflects surface impurities and was less reproducible than the advancing. This justifies, therefore, that advancing angles, representative of total surface energy of the solid, should be use to the calculations of surface free energy (Neumann and Spelt, 1996).

In the present study, for the material Kooliner, the water group showed an increase in total surface free energy through the increase of its polar component. The dispersive component suffered no changes, so we can deduce that Kooliner surface becomes more polar with water. According to Neves *et al.* (2013), the residual monomer molecules are replaced by the solvent molecules (Neves *et al.*, 2013) so, when this acrylic reline resin was treated with water, the molecule that replaced the residual monomer left was water, which has less volatility than ethanol, and material becomes more polar (Paraizo, 2012). Nevertheless, the surface free energy of Kooliner isn't affected by the post-polymerization treatment with 50% ethanol group, the treatment elected by Neves *et. al* (2013) as being the most effective on reducing residual monomer content of Kooliner (Neves *et al.*, 2013).

For the Ufi Gel Hard, differences between treatments groups were considered statistically significant but only in 70% ethanol solution they were found, showing lower values in total surface free energy and its polar component compared to the control group. Though, it was also found that the dispersive component showed an increase when specimens were treated with this solution. These two facts lead to the conclusion that this resin has a tendency to become more apolar with 70% ethanol solutions as post-polymerization treatment. Nevertheless, treatment with 70% ethanol solution was already considered inadequate to be used in this resin since Neves *et al.* (2013) found a significant decrease in mechanical properties, in spite of maximum removal of residual monomer. The surface free energy of Ufi Gel Hard isn't affected by

the post-polymerization treatment with 20% ethanol solution, the treatment elected by Neves *et. al* (2013) as being the most effective on reducing residual monomer content of this material (Neves *et al.*, 2013).

On Probase Cold, significant differences were found between the post-polymerization ethanol solutions applied, when total surface free energy was considered. This result are not similar to those found by Bettencourt et al. (2002) who demonstrated that ethanol does not considerably change the wettability properties of the MMA polymer (Bettencourt *et al.*, 2002). This can be explained by the different concentration of ethanol solutions used. The only difference observed is in the 70% ethanol solution as post-polymerization treatment that showed higher total surface free energy, but there were no significant differences in the dispersive component and in the polar component. This means that surface free energy is different when 70% ethanol solutions is used, but the balance between polar and dispersive components assures equilibrium.

At this point it may be conclude that the third hypothesis of this study could be rejected, since it was found effect of the 70% ethanol solutions as post-polymerization treatment in the surface free energy for Ufi Gel Hard.

The treatment proposed by Neves *et al.* (2013) continues to be feasible since in spite of differences found between treatment groups in the three materials surface free energy they are considered small in a clinical point of view. They probably do not affect the lubrification around the relining denture which may not lead to friction with adjacent tissues and, thus, paciente discomfort.

Surface energy is one of the main factors related to the development of denture related stomatitis (Minagi *et al.*, 1985). A controversial literature about the *Candida albicans* adherence exists so the effect of ethanol solutions as post-polymerization treatment on *Candida albicans* adhesion to acrylic reline resin surface remains to be investigated. In addition, others factores should also be considered, such as cell surface factores, diet, salivary composition and secretion rates, and antibody titers, which are all controlling factors in plaque formation and could therefore influence yeast attachment (Al-Dwairi *et al.*, 2012).

In the present study, the total surface free energy of Kooliner was lower than ones of Ufi Gel Hard and Probase Cold. Higher values of the dispersive component and similar of the polar component of Ufi Gel Hard can explain this result, concluding that

Ufi Gel Hard resin has a tendency to become more apolar than Kooliner. This can be explained possibly because of differences in the polymeric structure between these two resins. Ufi Gel Hard undergoes rapid polymerization reaction and solidifies quickly. It is likely that air voids are entrapped during mixing of the power and liquid components, which result in a porous structure (Urban *et al.*, 2007a; Urban *et al.*, 2009; Urban *et al.*, 2010). According to others studies, beyond the surface chemistry, wettability of a substrate is sensitive to the topographical texture (Meuler *et al.*, 2011) and this parameter must be considered when surface free energy data are evaluated (Kilani *et al.*, 1984).

The surface free energy of Kooliner and Probase Cold specimens showed differences. Probase Cold showed higher values in total surface free energy by the polar component than Kooliner and similar results in the dispersive component, so Probase Cold has a tendency to become more polar than Kooliner.

Other parameters must be evaluated in the future, such as the surface roughness and microbiological assays. Furthermore, it is important to note that information obtained from this test is limited and in future this should be complemented with other surface analysis technique, the X-ray photoelectron spectroscopy (XPS), for example.

At this point it was possible conclude that the fourth hypothesis of this study could be rejected, since Kooliner showed lower values of surface free energy than Ufi Gel Hard and Probase Cold.

The treatments proposed by Neves *et al.* (2013) continuing to be feasible, because enable the reduction of the monomer content and the biological effects, while keeping their properties, like microhardness, flexural strength, shear bond strength and surface free energy. This is a simple method and easy to achieve with equipment in a dental office to improve the biocompatibility of resins.

6. Conclusions

Within the limitations of this study, the main conclusions are:

- Post-polymerization treatment based on ethanol solutions did not negatively affected the shear bond strength between denture base and reline resins.

- The acrylic reline resins used influences the shear bond strength to denture base resin. Probase Cold revealed higher values of shear bond strength than Ufi Gel Hard and Kooliner, whose values were similar.

- The surface free energy of the reline resins is affected by the post-polymerization treatment. Mainly, the 70% ethanol solutions as post-polymerization treatment affected the surface free energy for Ufi Gel Hard.

- The values of surface free energy of three acrylic reline resins are different. Kooliner showed lower values of surface free energy than Ufi Gel Hard and Probase Cold.

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Appendices

Appendix 1 – Tables

Table 1 – Contact angle data for Kooliner.

CONTACT ANGLE (°)		*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
Water	***M ± SD***	79.96±4.00	72.04±3.43	78.87±2.82	79.12±3.10	75.09±2.96
	MIN	76.25	68.33	75.16	75.40	71.38
	MAX	83.67	75.16	82.58	82.83	78.80
1,2-propanediol	***M ± SD***	41.20±4.15	39.70±1.49	41.81±2.34	38.22±2.93	35.08±5.77
	MIN	36.67	35.16	37.28	33.68	30.55
	MAX	45.74	44.23	46.34	42.75	39.61

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

Table 2 – Contact angle data for Ufi Gel Hard.

CONTACT ANGLE (°)		*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
Water	***M ± SD***	65.89±7.16	64.27±4.81	69.44±2.75	75.29±2.79	85.16±6.34
	MIN	62.18	60.56	65.73	71.58	81.44
	MAX	69.60	67.98	73.15	79.00	88.87
1,2-propanediol	***M ± SD***	18.69±4.63	23.03±3.27	24.50±11.40	26.11±4.65	15.87±3.86
	MIN	14.16	18.50	19.97	21.58	11.33
	MAX	23.23	27.56	29.04	30.65	20.40

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

Table 3 – Contact angle data for Probase Cold.

CONTACT ANGLE (°)		*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
Water	***M ± SD***	70.46±3.04	70.42±5.10	71.35±1.93	67.26±4.32	64.96±4.09
	MIN	66.75	66.71	67.65	63.55	61.25
	MAX	74.17	74.13	75.07	70.97	68.68
1,2-propanediol	***M ± SD***	32.69±6.12	30.09±3.90	33.00±7.01	28.27±3.70	24.19±2.10
	MIN	28.26	25.56	28.46	23.74	19.66
	MAX	37.33	34.62	37.53	32.80	28.72

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

Table 4 – Surface free energy data for Kooliner.

SURFACE FREE ENERGY (γ) (mN/m)		*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
γTotal	***M ± SD***	32.93±1.72	36.68±1.77	33.17±1.32	33.70±1.50	35.89±1.67
	MIN	31.11	34.85	31.35	31.88	34.07
	MAX	34.76	38.50	34.99	35.52	37.72
γDispersive	***M ± SD***	17.46±1.89	16.33±0.68	16.96±0.86	18.21±0.95	18.26±1.84
	MIN	16.00	14.87	15.49	16.75	16.80
	MAX	18.93	17.79	18.42	19.68	19.73
γPolar	***M ± SD***	15.47±2.80	20.34±2.30	16.22±1.75	15.49±1.80	17.63±1.99
	MIN	13.00	17.87	13.74	13.01	15.15
	MAX	17.95	22.82	18.69	17.96	20.11

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

Table 5 – Surface free energy data for Ufi Gel Hard.

SURFACE FREE ENERGY (γ) (mN/m)		*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
γTotal	***M ± SD***	42.55±3.61	42.61±2.62	39.74±2.61	37.26±0.63	37.26±1.65
	MIN	40.72	40.79	37.92	35.44	35.43
	MAX	44.37	44.44	41.56	39.08	39.08
γDispersive	***M ± SD***	20.98±1.57	19.43±0.96	19.66±2.54	20.91±1.82	27.71±2.10
	MIN	19.51	17.97	18.20	19.45	26.25
	MAX	22.44	20.89	21.12	22.37	29.17
γPolar	***M ± SD***	21.57±4.83	23.19±3.25	20.08±0.96	16.35±2.24	9.55±3.48
	MIN	19.09	20.71	17.60	13.87	7.08
	MAX	24.05	25.66	22.55	18.83	12.03

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

Table 6 – Surface free energy data for Probase Cold.

SURFACE FREE ENERGY (γ) (mN/m)		*CONTROL*	*WATER*	*ETHANOL 20%*	*ETHANOL 50%*	*ETHANOL 70%*
γTotal	***M ± SD***	38.41±1.16	38.79±2.70	37.87±1.21	40.57±2.02	42.36±2.33
	MIN	36.59	36.97	36.05	38.75	40.54
	MAX	40.24	40.61	39.70	42.39	44.19
γDispersive	***M ± SD***	18.05±2.06	18.82±1.18	18.09±1.97	18.73±1.47	19.77±1.34
	MIN	16.59	17.36	16.23	17.27	18.32
	MAX	19.52	20.28	19.55	20.20	21.24
γPolar	***M ± SD***	20.36±2.73	19.97±3.40	19.79±1.76	21.83±3.27	22.58±2.65
	MIN	17.89	17.49	17.32	19.36	20.11
	MAX	22.84	22.44	22.27	24.31	25.06

M = Mean, SD = Standard deviation, Min = Minimum, Max = Maximum.

Appendix 2 – Figures

Figure 1 – Probase Hot (PH).

Figure 2 – Kooliner (K).

Figure 3 – Ufi Gel Hard (UGH).

Figure 4 – Probase Cold (PC).

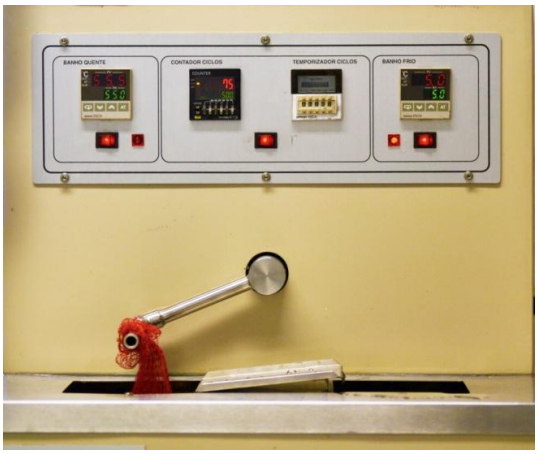

Figure 5 – Themocycling equipment.

Figure 6 – Ivomat pressure device.

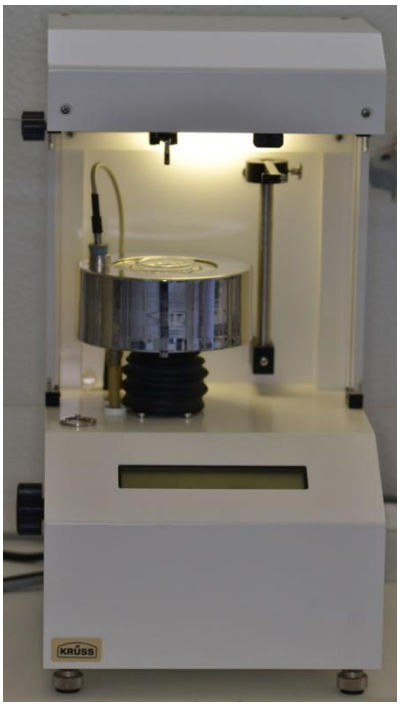

Figure 7 – Processor Tensiometer K12: Equipment used in Wilhelmy Plaque technique.

Figure 8 – Processor Tensiometer K12: Equipment used in Wilhelmy Plaque technique.

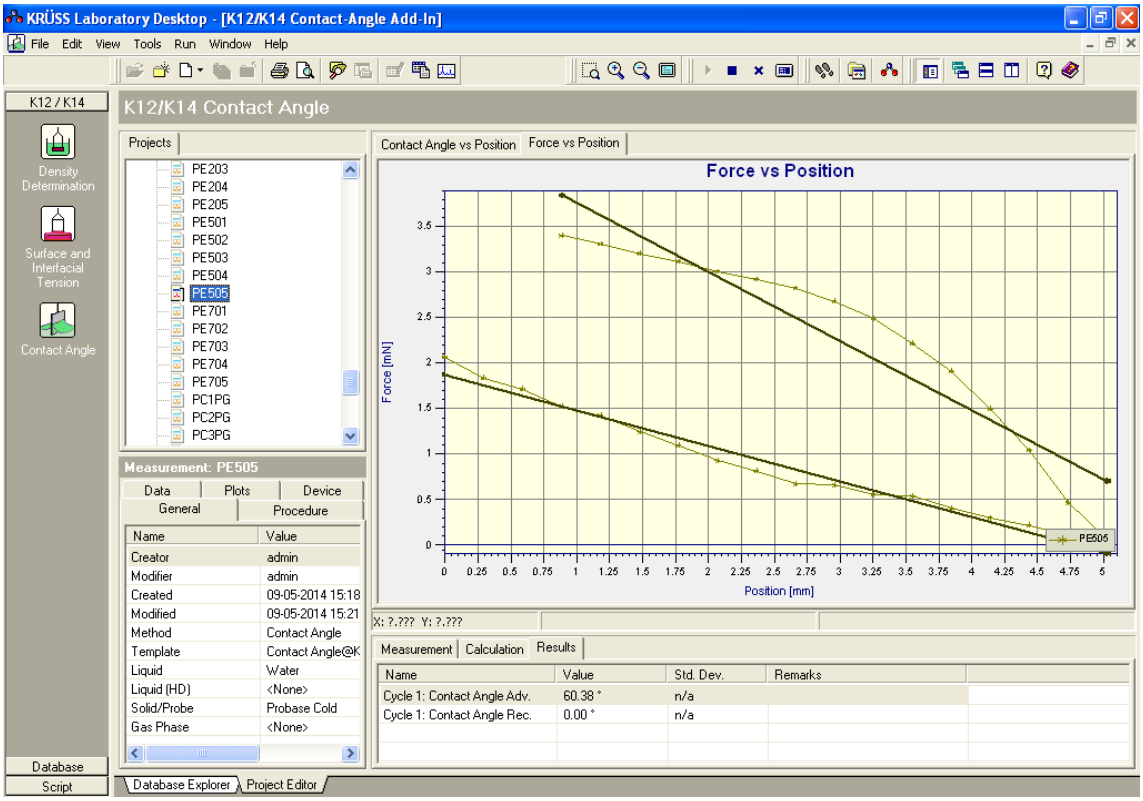

Figure 9 – KRUSS-software program: contact angle measuring system K121 (version 2.049).

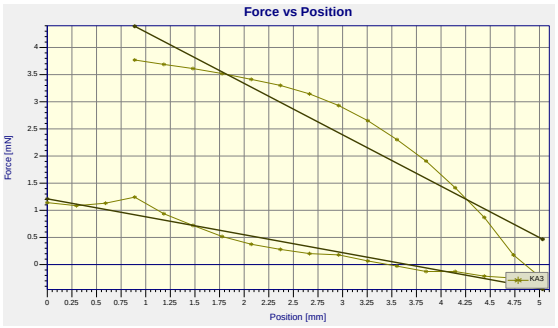

Figure 10 – One example of graphical obtained for determination of the contact angle of a Kooliner specimen.

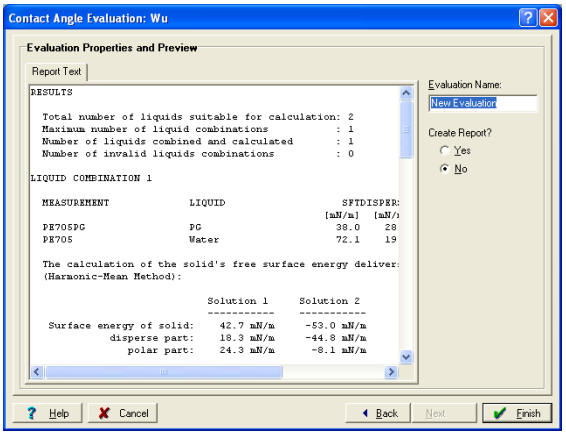

Figure 11 – One example of determination of the surface free energy of a Probase Cold specimen.

Appendix 3 – List of Tables

Appendix 4 – List of Figures

Appendix 5 – List of Abbreviations

1,6-HDMA	1,6-hexanedioldimethacrylate.
BMA	Butylmethacrylate
CON	Conditioner
HEMA	2-hydroxyethylmethacrylate
IBMA	Isobutylmethacrylate
K	Kooliner
L	Liquid
MMA	Methylmethacrylate
MPa	Megapascal
P	Powder
PC	Probase Cold
PEMA	Polyethylmethacrylate
PH	Probase Hot
PMMA	Polymethylmethacrylate
SF	Separating fluid
UGH	Ufi Gel Hard
XPS	X-ray photoelectron spectroscopy
γ	Surface free energy
γ^d	Dispersive component of surface free energy
γ^p	Polar component of surface free energy

Appendix 6 - Experimental Data

1. Shear bond strength

NUMBER SPECIMEN	MATERIAL	POST-POLYMERIZATION TREATMENT	SHEAR BOND STRENGTH (MPa)
1	Kooliner	Control	8,286
2	Kooliner	Control	2,269
3	Kooliner	Control	6,571
4	Kooliner	Control	7,393
5	Kooliner	Control	6,600
6	Kooliner	Control	5,370
7	Kooliner	Control	5,250
8	Kooliner	Control	3,026
9	Kooliner	Control	4,562
10	Kooliner	Control	2,348
11	Kooliner	Water	5,516
12	Kooliner	Water	5,116
13	Kooliner	Water	9,162
14	Kooliner	Water	6,034
15	Kooliner	Water	5,990
16	Kooliner	Water	3,640
17	Kooliner	Water	3,090
18	Kooliner	Water	2,163
19	Kooliner	Water	5,769
20	Kooliner	Water	7,050
21	Kooliner	Ethanol 20%	7,644
22	Kooliner	Ethanol 20%	7,627
23	Kooliner	Ethanol 20%	9,268
24	Kooliner	Ethanol 20%	1,814
25	Kooliner	Ethanol 20%	2,530
26	Kooliner	Ethanol 20%	6,260
27	Kooliner	Ethanol 20%	5,800
28	Kooliner	Ethanol 20%	5,268
29	Kooliner	Ethanol 20%	6,380
30	Kooliner	Ethanol 20%	3,224
31	Kooliner	Ethanol 50%	9,336
32	Kooliner	Ethanol 50%	7,562
33	Kooliner	Ethanol 50%	5,710
34	Kooliner	Ethanol 50%	8,985
35	Kooliner	Ethanol 50%	5,320
36	Kooliner	Ethanol 50%	7,340
37	Kooliner	Ethanol 50%	5,320

38	Kooliner	Ethanol 50%	2,075
39	Kooliner	Ethanol 50%	4,991
40	Kooliner	Ethanol 50%	2,969
41	Kooliner	Ethanol 70%	10,130
42	Kooliner	Ethanol 70%	14,970
43	Kooliner	Ethanol 70%	15,450
44	Kooliner	Ethanol 70%	5,600
45	Kooliner	Ethanol 70%	5,810
46	Kooliner	Ethanol 70%	3,420
47	Kooliner	Ethanol 70%	6,662
48	Kooliner	Ethanol 70%	4,285
49	Kooliner	Ethanol 70%	11,010
50	Kooliner	Ethanol 70%	3,651
51	Ufi Gel Hard	Control	11,450
52	Ufi Gel Hard	Control	6,611
53	Ufi Gel Hard	Control	11,010
54	Ufi Gel Hard	Control	6,980
55	Ufi Gel Hard	Control	5,170
56	Ufi Gel Hard	Control	5,750
57	Ufi Gel Hard	Control	4,531
58	Ufi Gel Hard	Control	3,445
59	Ufi Gel Hard	Control	6,801
60	Ufi Gel Hard	Control	4,326
61	Ufi Gel Hard	Water	1,971
62	Ufi Gel Hard	Water	7,690
63	Ufi Gel Hard	Water	9,265
64	Ufi Gel Hard	Water	3,230
65	Ufi Gel Hard	Water	6,810
66	Ufi Gel Hard	Water	2,550
67	Ufi Gel Hard	Water	2,945
68	Ufi Gel Hard	Water	4,615
69	Ufi Gel Hard	Water	4,486
70	Ufi Gel Hard	Water	4,098
71	Ufi Gel Hard	Ethanol 20%	5,643
72	Ufi Gel Hard	Ethanol 20%	11,290
73	Ufi Gel Hard	Ethanol 20%	4,087
74	Ufi Gel Hard	Ethanol 20%	6,680
75	Ufi Gel Hard	Ethanol 20%	4,690
76	Ufi Gel Hard	Ethanol 20%	3,170
77	Ufi Gel Hard	Ethanol 20%	4,516
78	Ufi Gel Hard	Ethanol 20%	4,501
79	Ufi Gel Hard	Ethanol 20%	3,747
80	Ufi Gel Hard	Ethanol 20%	3,240

81	Ufi Gel Hard	Ethanol 50%	4,323
82	Ufi Gel Hard	Ethanol 50%	7,300
83	Ufi Gel Hard	Ethanol 50%	12,470
84	Ufi Gel Hard	Ethanol 50%	11,080
85	Ufi Gel Hard	Ethanol 50%	4,610
86	Ufi Gel Hard	Ethanol 50%	7,270
87	Ufi Gel Hard	Ethanol 50%	3,749
88	Ufi Gel Hard	Ethanol 50%	3,186
89	Ufi Gel Hard	Ethanol 50%	6,629
90	Ufi Gel Hard	Ethanol 50%	3,793
91	Ufi Gel Hard	Ethanol 70%	11,800
92	Ufi Gel Hard	Ethanol 70%	8,095
93	Ufi Gel Hard	Ethanol 70%	10,740
94	Ufi Gel Hard	Ethanol 70%	10,160
95	Ufi Gel Hard	Ethanol 70%	8,490
96	Ufi Gel Hard	Ethanol 70%	7,140
97	Ufi Gel Hard	Ethanol 70%	5,440
98	Ufi Gel Hard	Ethanol 70%	8,440
99	Ufi Gel Hard	Ethanol 70%	4,768
100	Ufi Gel Hard	Ethanol 70%	8,998
101	Probase Cold	Control	26,740
102	Probase Cold	Control	14,700
103	Probase Cold	Control	13,670
104	Probase Cold	Control	26,230
105	Probase Cold	Control	8,050
106	Probase Cold	Control	10,590
107	Probase Cold	Control	7,488
108	Probase Cold	Control	15,120
109	Probase Cold	Control	13,400
110	Probase Cold	Control	10,660
111	Probase Cold	Water	18,730
112	Probase Cold	Water	8,908
113	Probase Cold	Water	16,110
114	Probase Cold	Water	27,840
115	Probase Cold	Water	15,730
116	Probase Cold	Water	16,860
117	Probase Cold	Water	17,610
118	Probase Cold	Water	6,386
119	Probase Cold	Water	7,079
120	Probase Cold	Water	15,960
121	Probase Cold	Ethanol 20%	13,570
122	Probase Cold	Ethanol 20%	24,660
123	Probase Cold	Ethanol 20%	11,780

124	Probase Cold	Ethanol 20%	21,760
125	Probase Cold	Ethanol 20%	26,720
126	Probase Cold	Ethanol 20%	10,650
127	Probase Cold	Ethanol 20%	8,580
128	Probase Cold	Ethanol 20%	10,920
129	Probase Cold	Ethanol 20%	8,733
130	Probase Cold	Ethanol 20%	17,740
131	Probase Cold	Ethanol 50%	20,370
132	Probase Cold	Ethanol 50%	13,320
133	Probase Cold	Ethanol 50%	14,780
134	Probase Cold	Ethanol 50%	20,360
135	Probase Cold	Ethanol 50%	14,640
136	Probase Cold	Ethanol 50%	19,790
137	Probase Cold	Ethanol 50%	18,020
138	Probase Cold	Ethanol 50%	9,737
139	Probase Cold	Ethanol 50%	8,051
140	Probase Cold	Ethanol 50%	11,410
141	Probase Cold	Ethanol 70%	20,750
142	Probase Cold	Ethanol 70%	8,996
143	Probase Cold	Ethanol 70%	9,254
144	Probase Cold	Ethanol 70%	12,440
145	Probase Cold	Ethanol 70%	2,300
146	Probase Cold	Ethanol 70%	18,720
147	Probase Cold	Ethanol 70%	19,160
148	Probase Cold	Ethanol 70%	15,450
149	Probase Cold	Ethanol 70%	9,919
150	Probase Cold	Ethanol 70%	17,920

2. Surface free energy

NUMBER SPECIMEN	MATERIAL	POST-POLYMERIZATION TREATMENT	MEASURES (mm)		
			WIDTH	HEIGHT	TICKNESS
1	Kooliner	Control	25,06	16,19	0,93
2	Kooliner	Control	24,42	17,84	1,01
3	Kooliner	Control	24,20	17,83	1,00
4	Kooliner	Control	25,18	18,48	1,02
5	Kooliner	Control	24,60	17,33	1,00
6	Kooliner	Water	24,29	18,68	1,01
7	Kooliner	Water	25,23	18,33	1,07
8	Kooliner	Water	25,15	16,61	1,07
9	Kooliner	Water	24,85	18,02	1,04
10	Kooliner	Water	25,13	18,71	1,06
11	Kooliner	Ethanol 20%	24,71	17,91	1,09
12	Kooliner	Ethanol 20%	25,20	18,90	1,05
13	Kooliner	Ethanol 20%	24,96	18,19	1,06
14	Kooliner	Ethanol 20%	25,05	17,74	1,07
15	Kooliner	Ethanol 20%	25,05	18,75	1,08
16	Kooliner	Ethanol 50%	24,82	18,07	1,03
17	Kooliner	Ethanol 50%	25,13	18,03	1,04
18	Kooliner	Ethanol 50%	25,01	18,87	1,02
19	Kooliner	Ethanol 50%	24,91	17,89	1,05
20	Kooliner	Ethanol 50%	24,75	17,85	1,00
21	Kooliner	Ethanol 70%	25,01	18,26	1,14
22	Kooliner	Ethanol 70%	24,57	18,81	1,09
23	Kooliner	Ethanol 70%	24,90	17,75	1,08
24	Kooliner	Ethanol 70%	25,25	18,46	1,12
25	Kooliner	Ethanol 70%	25,25	18,20	1,05
26	Ufi Gel Hard	Control	24,87	18,07	1,16
27	Ufi Gel Hard	Control	25,33	16,88	1,20
28	Ufi Gel Hard	Control	25,20	16,89	1,26
29	Ufi Gel Hard	Control	24,30	16,70	1,08
30	Ufi Gel Hard	Control	24,40	17,52	1,07
31	Ufi Gel Hard	Water	24,18	17,89	1,08
32	Ufi Gel Hard	Water	23,65	17,66	1,06
33	Ufi Gel Hard	Water	24,62	17,03	1,03
34	Ufi Gel Hard	Water	23,84	17,60	1,04
35	Ufi Gel Hard	Water	23,99	17,45	1,00
36	Ufi Gel Hard	Ethanol 20%	25,38	18,76	1,20
37	Ufi Gel Hard	Ethanol 20%	24,59	17,88	1,06
38	Ufi Gel Hard	Ethanol 20%	25,17	17,54	1,08
39	Ufi Gel Hard	Ethanol 20%	28,87	24,07	1,02

40	Ufi Gel Hard	Ethanol 20%	24,08	18,23	1,05
41	Ufi Gel Hard	Ethanol 50%	24,27	17,50	1,02
42	Ufi Gel Hard	Ethanol 50%	24,54	16,30	1,09
43	Ufi Gel Hard	Ethanol 50%	25,53	17,70	1,09
44	Ufi Gel Hard	Ethanol 50%	24,41	18,05	1,06
45	Ufi Gel Hard	Ethanol 50%	24,35	17,87	1,07
46	Ufi Gel Hard	Ethanol 70%	23,93	17,32	1,03
47	Ufi Gel Hard	Ethanol 70%	23,53	18,37	1,12
48	Ufi Gel Hard	Ethanol 70%	24,34	18,13	1,14
49	Ufi Gel Hard	Ethanol 70%	24,50	18,61	1,10
50	Ufi Gel Hard	Ethanol 70%	24,52	17,06	1,09
51	Probase Cold	Control	25,17	18,16	1,08
52	Probase Cold	Control	25,10	18,66	1,07
53	Probase Cold	Control	24,85	16,75	1,02
54	Probase Cold	Control	25,06	17,6	1,02
55	Probase Cold	Control	23,71	19,12	1,09
56	Probase Cold	Water	25,11	18,61	1,00
57	Probase Cold	Water	25,83	17,43	1,08
58	Probase Cold	Water	25,62	18,54	1,08
59	Probase Cold	Water	25,61	18,27	1,07
60	Probase Cold	Water	24,83	16,21	1,03
61	Probase Cold	Ethanol 20%	24,80	19,54	1,04
62	Probase Cold	Ethanol 20%	25,57	19,00	1,04
63	Probase Cold	Ethanol 20%	25,19	18,18	1,04
64	Probase Cold	Ethanol 20%	25,62	19,05	1,08
65	Probase Cold	Ethanol 20%	25,43	19,10	1,05
66	Probase Cold	Ethanol 50%	25,47	17,47	1,05
67	Probase Cold	Ethanol 50%	24,64	18,11	1,05
68	Probase Cold	Ethanol 50%	25,23	18,99	1,07
69	Probase Cold	Ethanol 50%	25,04	17,37	1,06
70	Probase Cold	Ethanol 50%	25,22	17,40	1,08
71	Probase Cold	Ethanol 70%	25,54	18,65	1,08
72	Probase Cold	Ethanol 70%	25,24	18,93	1,14
73	Probase Cold	Ethanol 70%	25,03	18,93	1,07
74	Probase Cold	Ethanol 70%	24,78	19,21	1,08
75	Probase Cold	Ethanol 70%	25,45	18,56	1,10

NUMBER SPECIMEN	MATERIAL	TREATMENT	ADVANCING CONTACT ANGLE (°)		SURFACE FREE ENERGY (mN/m)		
			WATER	1,2-PROPANEDIOL	TOTAL	DISPERSIVE COMPONENT	POLAR COMPONENT
1	Kooliner	Control	73,18	41,72	35,78	15,87	19,91
2	Kooliner	Control	82,32	34,55	33,27	20,31	12,96
3	Kooliner	Control	80,46	45,69	31,79	15,94	15,86
4	Kooliner	Control	80,41	43,21	32,24	16,79	15,45
5	Kooliner	Control	83,43	40,84	31,59	18,41	13,19
6	Kooliner	Water	67,42	40,15	39,05	15,47	23,58
7	Kooliner	Water	77,05	40,20	34,16	17,08	17,09
8	Kooliner	Water	71,32	37,06	37,32	16,97	20,34
9	Kooliner	Water	72,23	40,61	36,40	16,05	20,35
10	Kooliner	Water	72,17	40,46	36,45	16,09	20,36
11	Kooliner	Ethanol 20%	82,85	42,14	31,52	17,78	13,74
12	Kooliner	Ethanol 20%	75,64	43,31	34,35	15,79	18,56
13	Kooliner	Ethanol 20%	79,75	42,59	32,62	16,86	15,76
14	Kooliner	Ethanol 20%	79,34	43,29	32,67	16,53	16,14
15	Kooliner	Ethanol 20%	76,76	37,71	34,69	17,82	16,88
16	Kooliner	Ethanol 50%	75,73	34,64	35,63	18,55	17,08
17	Kooliner	Ethanol 50%	77,55	36,66	34,54	18,33	16,21
18	Kooliner	Ethanol 50%	77,46	41,20	33,82	16,83	16,99
19	Kooliner	Ethanol 50%	82,33	41,29	31,87	17,94	13,93
20	Kooliner	Ethanol 50%	82,51	37,29	32,63	19,42	13,22
21	Kooliner	Ethanol 70%	71,12	36,04	37,55	17,24	20,31
22	Kooliner	Ethanol 70%	77,33	26,60	36,36	21,29	15,07
23	Kooliner	Ethanol 70%	73,31	34,85	36,66	17,99	18,67
24	Kooliner	Ethanol 70%	75,29	35,08	35,75	18,32	17,42
25	Kooliner	Ethanol 70%	78,41	42,83	33,15	16,48	16,67
26	Ufi Gel Hard	Control	74,81	23,93	37,68	21,32	16,36
27	Ufi Gel Hard	Control	66,03	11,77	42,62	21,59	21,03
28	Ufi Gel Hard	Control	54,92	21,37	47,87	18,48	29,39
29	Ufi Gel Hard	Control	65,59	17,06	42,43	20,75	21,68
30	Ufi Gel Hard	Control	68,09	0,00	42,13	22,74	19,39
31	Ufi Gel Hard	Water	67,61	28,24	40,27	18,76	21,52
32	Ufi Gel Hard	Water	67,86	19,18	41,16	20,8	20,36
33	Ufi Gel Hard	Water	67,08	22,59	41,17	19,97	21,2
34	Ufi Gel Hard	Water	56,83	22,81	46,65	18,42	28,23
35	Ufi Gel Hard	Water	61,96	22,32	43,81	19,19	24,62
36	Ufi Gel Hard	Ethanol 20%	67,54	16,59	41,56	21,19	20,36
37	Ufi Gel Hard	Ethanol 20%	70,22	18,31	40,21	21,45	18,76
38	Ufi Gel Hard	Ethanol 20%	67,61	27,27	40,38	18,99	21,39
39	Ufi Gel Hard	Ethanol 20%	73,94	43,34	35,19	15,48	19,70

40	Ufi Gel Hard	Ethanol 20%	67,88	17,01	41,36	21,19	20,17
41	Ufi Gel Hard	Ethanol 50%	77,69	23,54	36,75	22,2	14,54
42	Ufi Gel Hard	Ethanol 50%	74,88	21,95	37,94	21,81	16,13
43	Ufi Gel Hard	Ethanol 50%	71,32	33,71	37,76	17,95	19,81
44	Ufi Gel Hard	Ethanol 50%	74,34	27,16	37,38	20,38	16,99
45	Ufi Gel Hard	Ethanol 50%	78,23	24,20	36,47	22,20	14,27
46	Ufi Gel Hard	Ethanol 70%	87,71	20,49	35,68	27,28	8,41
47	Ufi Gel Hard	Ethanol 70%	89,51	19,1	36,18	28,89	7,29
48	Ufi Gel Hard	Ethanol 70%	87,05	12,83	37,12	28,78	8,34
49	Ufi Gel Hard	Ethanol 70%	73,94	0,00	39,95	24,23	15,73
50	Ufi Gel Hard	Ethanol 70%	87,57	11,59	37,35	29,36	7,99
51	Probase Cold	Control	71,07	27,21	38,75	19,66	19,10
52	Probase Cold	Control	66,67	39,62	39,53	15,53	24,01
53	Probase Cold	Control	70,32	27,32	39,08	19,48	19,60
54	Probase Cold	Control	75,01	30,84	36,54	19,52	17,01
55	Probase Cold	Control	69,24	38,97	38,17	16,08	22,09
56	Probase Cold	Water	72,32	32,9	37,40	18,37	19,03
57	Probase Cold	Water	61,85	31,03	43,09	17,21	25,87
58	Probase Cold	Water	69,84	23,69	39,76	20,25	19,50
59	Probase Cold	Water	74,3	33,37	36,44	18,63	17,81
60	Probase Cold	Water	73,8	29,45	37,25	19,64	17,62
61	Probase Cold	Ethanol 20%	73,33	33,32	36,88	18,44	18,44
62	Probase Cold	Ethanol 20%	73,19	30,81	37,31	19,13	18,18
63	Probase Cold	Ethanol 20%	71,17	40,24	36,99	16,00	21,00
64	Probase Cold	Ethanol 20%	68,83	38,21	38,47	16,24	22,24
65	Probase Cold	Ethanol 20%	70,27	22,4	39,72	20,63	19,10
66	Probase Cold	Ethanol 50%	70,16	28,03	39,07	19,27	19,80
67	Probase Cold	Ethanol 50%	71,61	23,45	39,02	20,68	18,34
68	Probase Cold	Ethanol 50%	67,13	26,15	40,75	19,18	21,57
69	Probase Cold	Ethanol 50%	67,02	32,65	40,07	17,52	22,54
70	Probase Cold	Ethanol 50%	60,38	31,06	43,94	17,02	26,91
71	Probase Cold	Ethanol 70%	63,71	0,00	44,10	21,87	22,22
72	Probase Cold	Ethanol 70%	59,92	22,24	44,93	18,92	26,01
73	Probase Cold	Ethanol 70%	70,52	25,51	39,23	19,96	19,26
74	Probase Cold	Ethanol 70%	67,43	23,79	40,87	19,77	21,10
75	Probase Cold	Ethanol 70%	63,24	27,09	72,68	18,35	24,33